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(54) **Process for manufacturing a metallised polyolefin film and resulting film.**

(57) A process for manufacturing a metallised, flexible film of a polymeric material to provide a structure possessing high metal-to-film adhesion and little, if any, tendency toward metal fracture is disclosed. At least one polyolefin layer comprising a substantially isotactic polymer having a degree of atacticity of no more than 6% is subjected to flame treatment followed by vacuum metallisation of this surface (preferably with aluminium). The isotactic component is preferably polypropylene homopolymer. Other components include up to about 34% of an adhesive-promoting component which can be a C_2 to C_4 polymer, including a homo-, co-, or terpolymer, and a second isotactic polymer having a degree of atacticity from 6% to 15%.

EP 0 329 336 A2

PROCESS FOR MANUFACTURING A METALLIZED POLYOLEFIN FILM AND RESULTING FILM

This invention relates to processes for manufacturing metallized polymeric films as well as the films resulting from the process. More particularly, the invention provides metallized, for example aluminized, polymeric films wherein the metal-adherent surface comprises flame treated semi-crystalline polyolefin, such as isotactic polypropylene, containing from 0 to 50 weight percent of non-crystalline polyolefin component(s).

The metallization of polymeric films for aesthetic and/or functional purposes is a well developed technology. Thus, U.S. Patent 3,431,135 discloses a process for producing metallized linear polyester film which comprises passing a surface of a polyethylene terephthalate film through the primary cone of a flame produced by the combustion of a gaseous fuel mixture consisting essentially of oxygen and hydrocarbons, said fuel mixture having a fuel equivalence ratio greater than 1.0 and an oxygen ratio within the range of 0.26 and 0.30, and thereafter depositing on said surface a coating of aluminium deposited from a vapor thereof.

In accordance with the present invention, it has been found that a surface of a layer of a polymeric material comprising at least one semicrystalline polyolefin can be flame treated prior to vacuum metallization to provide a level of film-metal adherence which is significantly greater either than that achieved by corona discharge treatment of such a surface prior to vacuum metallization or by flame treatment of an essentially non-crystalline polyolefin homopolymer/copolymer surface.

In accordance with the present invention, there is provided a metallized flexible film which comprises at least one layer of a polymeric material, the layer comprising at least one semicrystalline polyolefin, preferably in an amount of at least 60 weight percent, most preferably at least 80 weight percent, of the composition of the layer, containing from 0 to 50 weight percent of an amorphous polyolefin and having a surface treated, prior to metallization of that surface, by exposure to flame to enhance significantly the adhesion of the metal to the surface.

Preferably, the semicrystalline polyolefin comprises a substantially isotactic homopolymer having a degree of atacticity no more than 6 percent and possessing an average xylene soluble content of not more than 10 weight percent (measured in accordance with FDA CFR Reg. 177.1520(c)1.1), especially polypropylene homopolymer. Advantageously, the semicrystalline polymer comprises polypropylene homopolymer which is from 80 to 100%, preferably from 95 to 96%, isotactic. When blends of isotactic homopolymer, such as polypropylene, are employed the blend preferably includes not more than 50 weight percent of a second isotactic homopolymer having a degree of atacticity of from 6% to 15%. The preferred polypropylene homopolymer possesses a melt index from 2 to 10 grams/10 minutes, and preferably a melt index from 3.5 to 6 grams/10 minutes.

In addition to the or each semicrystalline polymer the layer can also further comprise suitably not more than 34 weight percent, preferably not more than 20 weight percent, of a C_2 to C_4 polymer which promotes adhesion of metal to the surface of the layer. The C_2 to C_4 polymer may comprise a homo-, co-, or terpolymer; for example, a copolymer such as ethylene-propylene copolymer or ethylene-propylene-butene-1 terpolymer.

In one embodiment of the invention, the layer further comprises not more than 34 weight percent of a C_2 to C_4 polymer which promotes adhesion of metal to the surface of the layer and a second substantially isotactic homopolymer having a degree of acacticity from 6% to 15%, provided that the at least one substantially isotactic homopolymer is present in at least 50 weight percent.

Desirably, the treated surface is a gloss surface, preferably, wherein the surface possesses a gloss of at least 75%, most preferably at least 85%, at 45° (measured in accordance with ASTM-D245T).

The film can also include a core layer, one side of which is contiguous with the layer comprising at least one semicrystalline polyolefin, of isotactic polymer such as isotactic polypropylene homopolymer. The film can also include a heat sealable layer, one side of which is contiguous with the core layer.

This invention also provides a process for metallising a flexible film which comprises at least one layer of a polymeric material, which process comprises

(a) providing a layer comprising at least one semicrystalline polyolefin and containing from 0 to 50 weight percent of an amorphous polyolefin;

(b) treating a surface of the layer, prior to metallisation of that surface, by exposure to flame to enhance significantly the adhesion of the metal to the surface; and

(c) applying metal to the flame treated surface under vacuum metallising conditions.

Suitably, the semicrystalline polyolefin is a substantially isotactic polypropylene homopolymer. It is desirable that the film is oriented by stretching prior to steps (b) and (c). The flame treating of the surface

imparts an energy density from 30 to 60 dynes/cm to this surface, preferably from 35 to 55 dynes/cm.

This invention further provides the use of flame treatment to enhance the adhesion of metal to a surface comprising a major amount of a semicrystalline polyolefin.

In a preferred embodiment of the metallized, flexible film of the present invention, the film is provided as a laminate structure in which a core layer of substantially isotactic polypropylene is contiguous on one side with a layer comprising the same isotactic polypropylene of the core layer or a blend thereof with no more than 40 weight percent, and preferably no more than 20 weight percent, polyolefin copolymers and contiguous on the other side with a layer of heat sealable resin.

Suitable resins for use in any heat sealable layer include a blend of poly(1-butene) and a copolymer of ethylene or propylene and a higher olefin as disclosed in U.S. Patent 4,275,120; a blend comprising a copolymer of ethylene and a higher olefin and a different copolymer of higher olefins as disclosed in U.S. Patent 4,297,411; an interpolymer of propylene and two different higher alpha-olefins; a copolymer of butene-1 and a higher alpha-olefin or an interpolymer of ethylene, propylene and a higher olefin as disclosed in U.S. Patent 4,339,497; a heat-sealable acrylic resin on a primer layer as disclosed in U.S. Patent 4,439,493; and vinylidene chloride polymer on a primer layer as disclosed in U.S. Patent 4,495,027.

The laminate structure is advantageously fabricated by any conventional coextrusion procedure. In a typical structure, the coextruded laminate can have a total thickness of about 0.7 mils with the surface layers contributing from 2.5 to 9 percent of the total weight of the film. Following coextrusion, the laminate is biaxially oriented in a known manner and thereafter flame treated and vacuum metallized to provide a metallized, flexible film of this invention.

Flame treatment procedures contemplated include those disclosed in U.S. Patent 2,648,097; 3,028,622, 3,255,034, 3,347,697; 3,375,126; and 4,239,827. In one suitable type of flame treatment operation the surface of the oriented film which is to be metallized is continuously passed through, or in close proximity to, a flame at a rate sufficient to provide an exposure time from 0.0005 to 0.1 seconds. Typically, the intensity of the flame treatment is such as to impart an energy density of from 30 to 60 dynes/cm and preferably from 35 to 55, for example 45, dynes/cm, to the treated side(s) of the film.

Metallization is carried out in accordance with known vacuum metallization procedures using metals such as aluminium, zinc, copper (and alloys thereof such as bronze), silver and gold, aluminium being preferred for its economy, especially where packaging applications are concerned. A metal layer ranging in thickness from 100 to 500 angstroms is generally entirely suitable.

The resulting film possesses excellent metal to resin adherence as well as a high degree of resistance to metal fracture, especially in extrusion lamination with polyethylene. As such, the metallized film of this invention is particularly useful in flexible packaging applications to provide enhanced moisture barrier protection as well as an attractive appearance for the packaged goods.

The following Examples illustrate the invention.

EXAMPLE 1

A highly crystalline polypropylene homopolymer (melt flow of 4.2 and DSC melting point of about 162° C) core layer was coextruded with an upper metal-receiving layer of the same polypropylene and a lower heat sealable layer of a resin comprising ethylene-propylene copolymer containing 0.4 weight percent anti-blocking agents and 800 ppm erucamide and 100 ppm oleamide slip agents. The coextrudate was then quenched at 80° to 110° F, reheated to 240° to 280° F, and stretched in the machine direction 4 to 8 times using transport rolls operating at different speeds. After the desired machine direction orientation, the film was transversely oriented 7 to 10 times, at an appropriate temperature profile, in a tenter frame. The resulting film had an overall thickness of 0.80 mil with the core layer 0.63 mil, the top layer 0.03 mil and the bottom layer 0.14 mil. The upper layer was flame treated to various treatment levels (see Table 1).

The flame treated film was next metallized by vacuum deposition of aluminium and tested for metal pick off by SCOTCH 610 tape (3M Corp.). To test the metal adhesion, strips of SCOTCH 610 tape were applied to the metallized surface and the tape was pulled manually. At extreme testing conditions, the tape pull test was repeated three times with fresh tape applied to the same area. The metal pick-off was then recorded for comparison. Flame treatment samples with 33 to 40 dyne/cm treatment levels showed good metal adhesion after three SCOTCH 610 tape pull tests.

Table 1 shows the effect of various levels of flame treatment on the extend of metal pick-off.

Table 1

% Metal Pick-Off At Various Levels Of Flame Treatment	
Treatment (dynes/cm)	% Metal Pick-Off
33	30 to 50
34	20 to 40
36	20 to 50
38	15 to 50
40	40 to 50

COMPARATIVE EXAMPLE 2

The procedure of Example 1 was substantially repeated except that the upper layer of the stretched film was treated by corona discharge at various levels.

Table 2 shows the effect of corona discharge treatment on the percentage of metal pick-off. At every level of flame treatment carried out in Example 1, the resulting metallized film demonstrated significantly superior metal adhesion than the corona discharge treated film of this Example.

Table 2

% Metal Pick-Up At Various Levels Of Corona Discharge Treatment	
Treatment (dynes/cm)	% Metal Pick-Off
32	80 to 90
35	70 to 90
37	80 to 95
39	70 to 90

EXAMPLES 3 TO 10

Example 1 was substantially repeated with a variety of metal-receiving layer compositions. The flame treatment in each example was 38 to 40 dynes/cm. To test for observed metal fracture, the metallized film was laminated to another oriented polypropylene film employing a polyethylene adhesive. The polyethylene was cast at a 617° to 620° F stock temperature at 10 #/ream poly weight on the metallized film and subsequently laminated to the other oriented polypropylene substrate by a nip. The laminate was microscopically examined for metal fracture, a phenomenon which appears as the crazing of the metal.

The result of the metal fracture study are summarized in the following Table:

Table 3

Metal Fracture Observed With Various Metallized Substrates				
COMPOSITION OF METALLIZED LAYER OR FILM				
EXAMPLE	RESIN NO. 1	RESIN NO. 2	RESIN NO. 3	METAL FRACTURE
3	100	-	-	None
4	66	17	17	None
5	50	-	50	None
6	66	34	-	None
7	50	25	25	None
8	50	50	-	18%
9	-	100	-	18%
10	-	-	100	9.0%

RESIN NO. 1 = wt. parts highly crystalline polypropylene homopolymer having a xylene soluble content of about 3 to 4.5 wt. percent

RESIN NO. 2 = wt. parts amorphous ethylene-propylene copolymer

RESIN NO. 3 = wt. parts essentially amorphous crystalline homopolymer having a xylene soluble content of about 10 to 17 wt. percent.

As this data shows, metal-receiving layers based on at least 50 weight percent homopolymer containing an average xylene soluble content or not more than about 10 weight percent (Examples 3, 4, 5, 6 and 7) exhibited essentially no metal fracture. However, when the amount of homopolymer was less than 50 weight percent (Examples 8 and 9) or exceeded the foregoing average xylene soluble content (Example 10), an unacceptable level of metal fracture was observed.

Claims

1. A metallised, flexible film which comprises at least one layer of a polymeric material, the layer comprising at least one semicrystalline polyolefin containing from 0 to 50 weight percent of an amorphous polyolefin and having a surface treated, prior to metallisation of that surface, by exposure to flame to enhance significantly the adhesion of the metal to the surface.

2. A metallised film according to claim 1 wherein the semicrystalline polyolefin comprises a substantially isotactic homopolymer having a degree of atacticity of no more than 6 percent and possessing an average xylene soluble content of not more than 10 weight percent.

3. A metallised film according to claim 1 or 2 wherein the semicrystalline polyolefin is a substantially isotactic polypropylene homopolymer.

4. A metallised film according to any preceeding claim wherein the layer further comprises not more than 50 weight percent of a second substantially isotactic homopolymer having a degree of atacticity from 6% to 15%.

5. A metallised film according to any preceding claim wherein the layer further comprises not more than 34 weight percent of a C_2 to C_4 polymer which promotes adhesion of metal to the surface of the layer.

6. A metallised film according to claim 5 wherein the C_2 to C_4 polymer comprises a homo-, co-, or terpolymer.

7. A metallised film according to any preceding claim wherein the layer further comprises not more than 34 weight percent of a C_2 to C_4 polymer which promotes adhesion of metal to the surface of the layer and a second substantially isotactic homopolymer having a degree of atacticity from 6% to 15%, provided that the at least one substantially isotactic homopolymer is present in at least 50% by weight.

8. A metallised film according to any preceding claim wherein the treated surface is a gloss surface.

9. A metallised film according to claim 8 wherein the surface possesses a gloss of at least 75% at 45°.

10. A metallised film according to claim 9 wherein the surface possesses a gloss of at least 85% at 45°.

11. A metallised film according to any preceding claim which further comprises a core layer, one side of which is contiguous with the layer comprising at least one semicrystalline polyolefin.

12. A metallised film according to claim 11 which further comprises a heat sealable layer, one side of which is contiguous with the core layer.

13. A process for metallising a flexible film which comprises at least one layer of a polymeric material, which process comprises

(a) providing a layer comprising at least one semicrystalline polyolefin and containing from 0 to 50 weight percent of an amorphous polyolefin;

(b) treating a surface of the layer, prior to metallisation of that surface, by exposure to flame to enhance significantly the adhesion of the metal to the surface; and

(c) applying metal to the flame treated surface under vacuum metallising conditions.

14. A process according to claim 13 wherein the semicrystalline polyolefin is a substantially isotactic polypropylene homopolymer.

15. A process according to claims 13 or 14 wherein the film is oriented by stretching prior to steps (b) and (c).

16. A process according to any of claims 13 to 15 wherein flame treating of the surface imparts an energy density from 30 to 60 dynes/cm to this surface.

17. A process according to claim 16 wherein the energy density is from 35 to 55 dynes/cm.

18. A process according to any of claims 13 to 17 wherein the metal is aluminium.

19. A metallised flexible polymeric film comprising at least one layer possessing a glossy metal-receiving, polyolefin surface, said polyolefin containing at least 50 weight percent of a homopolymer and possessing an average xylene soluble content of not more than 10 weight percent.

20. The use of flame treatment to enhance the adhesion of metal to a surface comprising a major amount of a semicrystalline polyolefin.